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Technical Paper 342

DEPARTMENT OF THE INTERIOR
HUBERT WORK, SECRETARY
BUREAU OF MINES
H. FOSTER BAIN, DIRECTOR

METHODS FOR THE RECOVERY OF PLATINUM, IRIDIUM, PALLADIUM, GOLD, AND SILVER FROM JEWELERS' WASTE

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BY

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WASHINGTON
GOVERNMENT PRINTING OFFICE
1924

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First edition, January, 1924.

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METHODS FOR RECOVERY OF PLATINUM, IRIDIUM, PALLADIUM, GOLD, AND SILVER FROM JEWELERS' WASTE.

By C. W. Davis.

INTRODUCTION.

Because of the extensive use of platinum and white gold in jewelry, the Bureau of Mines has received numerous inquiries concerning the recovery of the valuable metals from scrap, filings, sweeps, and other waste. This paper has been prepared in an attempt to answer these inquiries. Although the necessary manipulations and the chemical procedures are discussed in a rather elementary manner in order to enable persons who have had only a little laboratory experience to use some of the methods, the separation and recovery of the platinum metals is intricate and should be performed only by a skilled chemist. For this reason it is advisable either to employ such a chemist or to ship the material to one of the many refiners of platinum.

METALS TO BE RECOVERED.

Platinum, gold, and silver, and alloys containing two or more of the metals mentioned here—platinum, iridium, gold, palladium, silver, copper, nickel, zinc, and manganese—are likely to be present in material from which the jeweler wishes to recover the valuable metals. Certain mixtures of these metals and alloys may be treated more easily than others; consequently the methods for the recovery of the metals are separated into classes, as shown in the accompanying table. Especial attention is called to case 1, where group separations only are required. Here, any or all of the valuable metals may be present either free or alloyed except that if alloyed the alloy or alloys containing one or more of the metals platinum, iridium, and palladium must be free from gold, silver, or appreciable amounts of copper and zinc; and the alloy or alloys containing gold, silver, and base metals must be free from platinum, iridium, and palladium. The separation will recover platinum, iridium, and palladium in one group, and gold, silver, and base metals in another group. This method depends on the fact that gold, silver, and base metals alloy directly with mercury to form amalgams, but the other metals form

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an alloy only under certain conditions, such as in the presence of zinc amalgam, acid, and copper sulphate. Zinc or tin must be absent, as an amalgam would be formed with them and the platinum-group metals would go with the amalgam.

In the use of Table 1 it will be found that the less complex methods apply when the valuable metals are not alloyed either with themselves or with the base metals.

TABLE 1.—*Procedures that apply when certain metals are present.*

[Au, gold; Ag, silver; Pd, palladium; Pt, platinum; Ir, iridium; base metals—copper, nickel, zinc, etc.]

Case.	Metals present.		See note—	Procedures that apply. (See pp. 6 to 14.)
	Not alloyed.	Either free or alloyed.		
1		Pt, Pd, Ir, Au, Ag, base metals	A	*f*, *g*, and *k*.
2	Au, Ag	base metals	B	*a*, *b*, *c*, and *g*.
3		Au, Ag, base metals	B	*l*, *a*, *b*, and *c* or *t*.
4	Pt, Au	base metals	B	*m* and *n* or *f*, *g*, and *k*.
5	Pt, Ag	do	B	*a*, *b*, *c*, and *g*.
6	Pt, Au, Ag	do	B	*a*, *b*, *c*, *m*, and *n* or *f*, *g*, *k*, *a*, *b*, and *c*.
7	Pt, Au	Ag, base metals	B	Do.
8	Pt, Ag	Au, base metals	B	Do.
9	Pt	Au, Ag, base metals	B or C	*f*, *g*, *k*, *l*, *a*, *b*, and *c*; or *t*.
10	do	do	C	*a*, *b*, *c*, *m*, and *n*.
11		Pt, Au, Ag, base metals	B	*o* or *t*.
12	Au	Pd, Ag, base metals	B	*a*, *b*, *c*, *d*, *i*, and *j* or *r*.
13	Pt	do	B	Do.
14	Pt, Au	do	B	*a*, *b*, *c*, *d*, *i*, *j*, *m*, and *n*.
15	do	do	B	*a*, *b*, *c*, *d*, *i*, *j*, *f*, *g*, and *k*.
16	Pt	Pd, Au, Ag, base metals	B	*f*, *g*, *k*, *l*, *a*, *b*, *c*, *d*, and *r* or *i* and *j*.
17		do	B	*l*, *a*, *b*, *c*, *d*, and *r*, or *i* and *j*; or *t*.
18		Pt, Pd, Au, Ag, base metals	B	*o*, *p*, and *q* or *r*; or *t*.
19	Au, Ag	Ir, Pt	B	*a*, *b*, *c*, *f*, *k*, and *s*.
20	Ag	do	B	*a*, *b*, *c*, and *s*.
21	Au	do	B	*f*, *k*, and *s*.
22		Pt, Pd, Ir, Au, Ag, base metals	B	*s*.
23	Au	Ir, Pt, Ag, base metals	B	*m*, *n*, and *s*.
24	Au, Ag	Ir, Pt, Pd	B	*f*, *g*, *k*, *a*, *b*, *c*, and *s*.
25	Ag	do	B	*f*, *k*, and *s*.
26	Au	do	B	Do.

NOTES.—A. Any or all of the valuable metals may be present, either free or alloyed, in any proportion, except that if alloyed the alloy or alloys containing one or more of the metals platinum, iridium, and palladium must be free from gold, silver, or appreciable amounts of copper and zinc; and the alloy or alloys containing gold, silver, and base metals must be free from platinum, iridium, and palladium. Zinc or tin must be absent. The separation will recover platinum, iridium, and palladium in one group and gold, silver, and base metals in the other group, the separate metals being recovered, if desired, by suitable methods selected from the table.

B. The metals named in the third column may be free or alloyed in any proportion.

C. The same as B except that when silver is alloyed with gold the ratio of silver to gold must be 3 or more to 1, or else the quantity of silver must be small.

GENERAL INFORMATION.

TESTS TO DETERMINE CLASS OF MATERIAL.

CLASS A.

Platinum, iridium, and palladium, either free or alloyed, do not amalgamate directly with mercury, but if other metals such as gold, silver, copper, and zinc, which form amalgams directly, are alloyed with the previous metals the latter alloy will be held by the mercury and no separation will be obtained by the procedures outlined in case

1 (see Table 1). The absence of zinc and tin must be assured, as an amalgam of these metals, formed on treatment with mercury, will stick to platinum-group metals.

A small portion of the well-mixed material is treated by methods *f* and *k* (see pp. 8 and 9). The residue from *k* is treated by method *o*. If there is no platinum, iridium, and palladium in the retort residue from *k* the material comes in this class.

CLASSES B AND C.

A small amount of the material is warmed with dilute nitric acid (1 part acid to 4 parts water) in a beaker until the action is complete. The solution is poured away from the residue, fresh acid added, and the heating repeated as long as any action is seen to take place. The residue is then washed with water three times, aqua regia added, the beaker warmed until action has become slow, and the solution then poured away from the metal. The residue is treated with fresh aqua regia and the above process repeated until there is no further dissolving action. If this treatment dissolves all the metallic portion of the sample or leaves white metallic particles as a residue the material may be considered in class C. If the gold-silver alloy in the sample becomes coated with a dull layer (silver chloride) on treatment with aqua regia the material belongs in class B. If the ratio of silver to gold in an alloy of these metals is less than about 3 to 1, nitric acid will not dissolve all the silver. If the ratio of silver to gold is less than this the gold in the residue from a nitric-acid extraction will not be dissolved by aqua regia unless the silver content is very low, because a protective coating of silver chloride forms on the surface of the metal and prevents further action.

GRANULATION OF ALLOYS.

The rate of solution of alloys depends on the size of the pieces to be dissolved. To facilitate the solution of metals, especially when it is permissible to melt them, the following procedure should be used: The molten metal is thoroughly stirred and is then poured with a circular, wavy motion in a thin stream (to prevent the formation of lumps) into a tank filled with cold water; the water may be kept cold by means of ice or a stream of water. The pouring should be done about 3 feet above the surface of the water. The tank may be fitted with a perforated pan which is lifted out when the pouring is completed, and the granulations, which are flaky or form small hollow spheres, are allowed to drain.

REAGENTS AND SOLUTIONS USED.

Although technical grades of chemicals may be used for some of the procedures it is safer to obtain chemically pure (C. P.) reagents from a chemical supply house. For example, if the nitric acid used to dissolve silver has hydrochloric acid as an impurity, silver chloride will be precipitated and gold dissolved. This acid, however, is satisfactory for the preparation of aqua regia. All solutions should be thoroughly mixed before using. Ferrous-sulphate solution is prepared by dissolving ferrous sulphate in distilled water to form a strong solution. This should be prepared freshly each time it is used, as it is oxidized in the air and thus made useless. The stock of ferrous sulphate from which the solution is made should be kept in a tightly stoppered bottle.

Ammonium-chloride solution (saturated) is prepared by adding ammonium chloride to distilled water until no more will go into solution.

Sodium-chloride solution may be prepared by dissolving sodium chloride in distilled water.

Nitric acid (1 to 4) is prepared by adding 1 volume of concentrated (C. P.) acid to 4 volumes of distilled water.

Aqua regia is prepared by mixing 3 volumes of hydrochloric acid (C. P.) and 1 volume of nitric acid (C. P.). Aqua regia (1 to 5) is prepared by mixing 1 volume of aqua regia and 5 volumes of distilled water.

Sodium-hydroxide solution is prepared by dissolving sodium hydroxide (C. P.) in distilled water.

Ammonium hydroxide (1 to 3) is prepared by mixing 1 volume of concentrated ammonium-hydroxide solution (C. P.) with 3 volumes of water.

Stannous-chloride solution is prepared by dissolving a convenient weight of stannous chloride (C. P. $SnCl_2 . 2H_2O$) in twice its weight of water and adding a little hydrochloric acid (about 5 per cent).

The zinc for precipitating platinum is preferably 20 mesh (C. P.). The zinc for precipitating gold may be of technical grade.

Formic acid and sodium carbonate should be chemically pure.

Copper sulphate–sulphuric acid solution for use in method *g* may be prepared by dissolving 1 gram of copper sulphate and 1 gram of sulphuric acid in 2 liters of water. Zinc amalgam can be purchased from a chemical supply house or may be prepared by pouring molten zinc into mercury until the cooled amalgam is solid. The solid amalgam is then pulverized in a mortar.

TESTING SOLUTIONS FOR GOLD, PLATINUM, AND PALLADIUM.

About 1 ounce of the solution to be tested is poured into a test tube or beaker and a few drops of stannous chloride solution added. If platinum or iridium is present a yellow or red tint will develop for about 15 minutes, the color depending on the quantity present; if palladium is present the color is yellow or brown; and in the presence of gold a purple or brown color or brown precipitate will form, depending on the acidity and concentration. The tests should be tried with solutions known to contain the metals so that the operator may learn what to expect.

APPARATUS.

Glass or porcelain containers should be used for solutions that contain acid. Pyrex chemical glassware or Coors chemical porcelain should be specified, as these brands have the greatest mechanical strength and are not affected by the temperature changes that necessarily occur. Glass beakers should be used for solutions in operations that involve precipitation, filtration, and boiling; porcelain evaporating dishes are best for evaporating solutions. A sand bath or water bath should be used for heating, boiling, or evaporating liquids. A sand bath may be made by filling an iron dish with sand. The container to be heated is set in the sand and heat applied to the bottom of the pan. A water bath is a covered shallow tank or dish partly filled with water with holes cut in the cover to receive the containers to be heated. Heat is applied at the bottom. Such a bath permits uniform, regulated heating.

Stirring rods made of glass rods or tubing are convenient for agitation.

This and other equipment, such as wash bottles, mercury retorts, " gold pans," funnels, and filter paper, can be obtained from chemical or metallurgical supply houses.

MANIPULATIONS.

EVAPORATION.

Evaporations are most rapid when performed in evaporating dishes (beakers may be used) on a sand bath at rather high temperature to remove the bulk of the solution, finishing over a water bath when the material gets thick, begins to spatter, or is almost dry.

DISSOLVING METALS.

The rate at which metals dissolve in acids is determined by the size of the particles and by the quantity of acid left in the solvent. The quickest method therefore is to treat the finely divided metal with an acid and when the action has become slow to pour off the solution and add a fresh lot of acid, then repeat until the metal is dissolved.

SEPARATING PRECIPITATES FROM LIQUIDS.

In separating a precipitate (a solid) from a liquid and in washing the precipitate it is best to let the precipitate settle and then, if the solution above it is perfecly clear, to siphon or pour off the clear solution, add the washing solution to the residue, mix, let the residue settle and again pour off the clear solution; repeat several times and pour off as much liquid as possible each time without removing the precipitate. If the precipitate does not settle so as to leave a clear solution, the solution is decanted through a filter paper supported on a glass funnel, and as much precipitate as possible is left in the dish. The latter is washed by decantation as before. The final washing in either method is best performed by rinsing the precipitate into the filter paper and washing with a stream of washing solution, letting all of the solution drain through the paper before fresh washing solution is added.

PANNING.

Panning—the separation of light foreign material from heavier valuable matter—is performed by placing the sample in a "gold pan" (a flat pan with flaring sides) and adding water. The material is then mixed until completely wet; any floating particles are forced under the surface with the fingers. The pan is then given a gyratory motion and after the heavier particles have been allowed to settle for a moment the water carrying the lighter material is poured off. Fresh water is then added and the process repeated until a good concentration has been effected. If the foreign matter is not finely divided it should be ground in a mortar before panning is begun. A stream of water will sometimes help wash the foreign matter away from the metals. By another method the edge of the pan containing the sample is dipped into an auxiliary pan full of water. A jerking motion of the pan holding the sample will help to wash away the lighter material. A little practice will enable one to make a clean separation by panning.

METHODS OF PROCEDURE.

If the material to be treated is contaminated by dirt or iron filings most of the former may be removed by panning and the latter by picking up the magnetic particles with a magnet.

METHOD *a* (CHEMICAL).

The material—filing, scrap, or concentrated sweeps—is warmed with dilute nitric acid (1 to 4) in a covered beaker or dish. After all dissolving action has ceased—indicated by the evolution of bubbles stopping—the solution is decanted or filtered into another beaker and the residue is treated with a fresh portion of the dilute acid as before. This treatment is repeated as long as any action is seen when the solution is warmed with fresh acid. The temperature to which the solution is heated should not be too high or boiling may be mistaken for dissolving action and more acid used than is necessary. About 3 pounds of concentrated nitric acid are required for each pound of metal; the quantity, of course, depends on the amount of soluble metals present.

The final residue is washed with distilled water several times by decantation through a filter. The residue from metals included in cases 2, 3, and 12 (see Table 1, p. 2) and method *l* (p. 9) contains gold free from silver and base metals; from cases 5 and 13, platinum free from silver and base metals; from cases 6, 7, 8, 14, and 15 gold and platinum free from silver and base metals; and from cases 19, 20, 22, etc., platinum and iridium, with or without gold, and free from silver and base metals. If contaminated with dirt the residue may be treated by methods *g* and *k*, or *h*, *i*, and *j*.

METHOD *b* (CHEMICAL).

The solution and wash waters—which may contain silver, platinum, palladium, and base metals—are mixed and a solution of sodium chloride is added a little at a time with constant stirring until a fresh addition of the solution causes no further precipitation. The white precipitate formed contains the silver as chloride. After the mixture has settled for an hour or more the silver salt is removed by filtration through a filter paper and is thoroughly washed with hot distilled water, first by decantation, then on the filter.

METHOD *c* (CHEMICAL).

If the silver salt is white or purple (it turns purple when exposed to light) it may be considered free from palladium, and if the original material contained no silver-platinum alloy in which the ratio of silver to platinum was high, the precipitate will be free from platinum. The precipitate, if it contains no platinum, is put in a dish with some distilled water and enough sulphuric acid and granulated zinc is added to reduce the silver chloride to the metal. One-third pound of sulphuric acid (conc.) and one-fourth pound of zinc will reduce the silver from 1 pound of silver chloride. When the reduction is completed the silver is allowed to settle, treated with a little more acid to dissolve any residual zinc, filtered, washed with hot water, dried, and melted with borax glass to obtain the compact metal. (See method *e*, p. 7.)

METHOD *d* (CHEMICAL).

If the silver salt obtained by method *b* is pink the presence of palladium is to be suspected; if the original material contained an alloy of platinum and silver in which the ratio of silver to platinum was high (10 or more to 1) some of the platinum that would be dissolved may be held in the silver precipitate. To separate the silver from these metals the precipitate is treated with enough ammonium hydroxide solution (1 to 3) to give a clear solution. The solution is diluted with about twice its volume of distilled water and nitric acid is added slowly until all the silver is reprecipitated. The silver chloride is caught on a filter paper, washed, and treated as in method *c*. (See also method *e*).

METHOD *e* (CHEMICAL).

If the presence or absence of palladium and platinum is not known, the solutions left from *c* or *d* are tested for the presence of these metals with stannous chloride solution (see "General Information," p. 2). If no valuable metals are present the solutions are discarded. If either platinum or palladium is present in solution without the other it may be recovered as shown in methods *i* and *j;* or *p* or *r*. If both of the metals are present in the solution they may be removed by methods *p*, *q*, and *r*.

METHOD *f* (AMALGAMATION).

The residue from *a* or the filings, scraps, or concentrated sweeps, as the case may be, are put in a dish. Enough mercury to form a liquid amalgam (about 5 parts of mercury to 1 part of the sample, by weight) and water are added and the dish is agitated from time to time during one-half hour or more. The material may also be agitated by putting it in a bottle and rolling the bottle. If the mercury becomes finely divided and the minute globules will not combine, a few drops of sodium hydroxide solution or sulphuric acid are added to remove from the surface of the particles the film that prevents consolidation.

The amalgam containing all the metals except those of the platinum group (platinum, palladium, and iridium) is carefully poured away from the residue which will contain platinum (or the platinum metals), either clean or mixed with dirt, depending on the material treated. The residue is washed away from the amalgam by a stream of water from a wash bottle and by proper manipulation of the dish (see "Panning," p. 6).

The amalgam is treated by method *k*. If the material treated be scraps, turnings, drillings, or filings the residue from method *f* will be pure platinum or platinum metals. If, however, such material as sweepings is treated by this method the residue will contain dirt which may be separated by *g* or *h*, *i*, and *j*.

METHOD *g* (AMALGAMATION).

Dirt may be separated from the platinum metals or gold by panning, or the metals may be separated by melting with borax glass, by amalgamation, or by chemical treatment. For gold the procedure is the same as that given in *f* and *k*. For platinum or an alloy of platinum that is not picked up by mercury, the same method is used except that one-fifth pound (or more) of zinc amalgam is added for every pound of mercury and instead of water an aqueous solution containing about 0.05 per cent of copper sulphate and 0.05 per cent (by weight) of sulphuric acid is used. Under these conditions the platinum metals will be held by the mercury and can be removed from the foreign material by panning. (See "General Information," p. 2, for the preparation of the copper sulphate and sulphuric acid solution and the zinc amalgam.)

METHOD *h* (CHEMICAL).

Another method of separating dirt from platinum or gold is to heat the residue with aqua regia, pour off the solution from time to time and add fresh aqua regia. This procedure will dissolve the platinum or gold and leave most of the foreign matter behind. When it is free from metallic platinum or gold, the residue is separated by filtration, washed thoroughly with hot distilled water, and discarded. The gold or platinum is then recovered from solution by methods *i* and *j*.

METHOD *i* (CHEMICAL).

The solution is evaporated just to dryness on a water bath;[1] moistened with hydrochloric acid, and extracted with distilled water. This treatment removes most of the nitric acid and puts the material in a condition so that the platinum, palladium, or gold may be completely removed by methods *j*, *n*, *p*, or *r*.

METHOD *j* (CHEMICAL).

Granulated zinc (20-mesh, C. P.) is added and after enough hydrochloric acid to cause the evolution of bubbles from the zinc has been added the reaction is allowed to run to completion, more hydrochloric acid being added until all the zinc has been dissolved. The finely divided black precipitate of platinum or palladium is caught on a filter and washed first with dilute hydrochloric acid (1 to 10), then with distilled water. Copper if present in the solution would be precipitated with the platinum metal and remain as an impurity. The copper may be removed from the platinum metal by the method given in *r*.

A small amount of the solution is tested for platinum or palladium (see "General Information," p. 2), and if either is present more zinc is added to the solution and wash waters and the procedure is repeated. If the solution contains no platinum or palladium it is discarded. An alternate procedure for the precipitation of palladium and platinum free from copper is given in method *r* (p. 12).

METHOD *k* (AMALGAMATION).

The amalgam obtained in *f* is squeezed through chamois leather or a closely woven cloth, such as canvas. The mercury that goes through still contains some of the valuable metals but may best be saved for the treatment of fresh batches of material. The solid amalgam that does not go through the chamois is wrapped in two or three thicknesses of paper and placed in a cast-iron mercury retort and heated, at first slowly, to the boiling point of mercury. After the bulk of the mercury has been distilled and collected the heat is gradually increased until the retort is bright red. The mercury, which is condensed by passing the vapor from the retort through cooled tubes, can be used again. The ash formed from the paper keeps the residual metal from becoming attached to the retort.

The residue is treated for the metals contained, by the methods indicated in Table 1.

METHOD *l* (INQUARTATION AND GRANULATION).

If the ratio of silver to gold is not already 3 to 1 or more, enough silver to make it so is added and the material is melted and stirred to form a homogeneous melt. The molten material is granulated (see "General Information," p. 2) and treated by methods *a*, *b*, and *c*. The forming of a gold-silver alloy by the addition of silver is known as inquartation.

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[1] **Sand bath may be used at first to decrease the time required, but should be replaced, before the solution is all removed, by a water bath, to prevent heating to a temperature that would make the residue insoluble.**

METHOD *m* (CHEMICAL).

The residue from method *a*, or original material, is warmed for some time with fresh portions of dilute aqua regia (1 to 5) which will dissolve the gold and leave the platinum, iridium, or silver in the residue. While the substance is being heated with aqua regia (1 to 5) its temperature should be raised gradually and when the evolution of bubbles has become rapid the temperature should not be increased very much; otherwise platinum will be dissolved.

In case 6 (see Table 1, p. 2) the residue will be pure platinum or platinum mixed with dirt. The solution will contain gold which may be recovered by method *n*. After the gold has been dissolved the residue is washed with distilled water and, if the material contained a gold-silver alloy low in silver, extracted with a solution of ammonium hydroxide (1 to 3). This solution will dissolve any silver which would be present as chloride at this stage. The metal is removed by filtering and if mixed with dirt may be treated as shown in method *g* or methods *h* and *i*. The silver, which is again precipitated as the chloride from the ammonium hydroxide solution by the addition of nitric acid, is filtered off and recovered as shown in method *c*.

METHOD *n* (CHEMICAL).

The solution from *m*, containing the gold and base metals and possibly a little platinum and silver, is evaporated just to dryness on a water bath in order to remove nitric acid. A little hydrochloric acid and distilled water, enough to give a convenient volume are added, and any residue of silver chloride is removed by filtering. Ferrous sulphate equal to five times the weight of the gold to be recovered is dissolved in distilled water and added. The mixture is then warmed on a sand bath, but not heated to boiling, and the gold is precipitated, washed with water by decantation through a filter, dried, and melted with borax glass. The solution is tested for gold by the stannous chloride reaction (see "General Information," p. 2). If gold is present, more ferrous sulphate is added and the solution again heated to remove the rest of the gold. If platinum is shown to be present by test, it is recovered with zinc as shown in method *j*.

METHOD *o* (INQUARTATION AND CHEMICAL).

The material is melted with enough silver to make the ratio of silver to gold at least 3 to 1 and the ratio of silver to platinum at least 15 to 1 and is then granulated (see "General Information," p. 2). The granules are extracted with dilute nitric acid (1 to 4) as explained in method *a*, which dissolves all the silver, palladium, and base metals and most of the platinum, if these metals are present. The solution is filtered and the residue washed thoroughly with distilled water. The solution, which may contain silver, palladium, platinum, and base metals, is treated with a sodium chloride solution to recover the silver, as shown in method *c* or *d*, and the palladium and platinum are recovered in *p*. If platinum metals are absent the residue will be metallic gold which may be melted with borax directly. If the residue contains gold and platinum it is extracted with dilute aqua regia (1 to 5), as explained in method *m*, leaving metallic platinum.

When material is tested for class A any metallic residue at this point indicates the presence of platinum metals. The gold and any dissolved platinum is recovered from the solution as explained in *n*.

METHOD *p* (CHEMICAL).

To recover the platinum and palladium from the solution obtained in *e*, *o*, etc., hydrochloric acid is added and the material evaporated just to dryness on a water bath. A sand bath may be used at first, but heating the dry residue much above the boiling point of water should be avoided as it will make the platinum residue insoluble. Enough hydrochloric acid to moisten the precipitate is then added and the residue taken to dryness as before. The residue is moistened again with hydrochloric acid and just enough water is added to dissolve the residue. Then ammonium chloride crystals are added until the solution is saturated.

After the solution has stood overnight, the precipitate which contains platinum as ammonium chloroplatinate, is caught on a filter and washed with a 20 per cent solution of ammonium chloride. The platinum salt is dried and ignited carefully, first in a closed then in an open crucible. The platinum is thus recovered as metallic sponge platinum.

The solution may be treated at once to recover the palladium, but if the quantity of palladium and copper is not large it is better to evaporate the excess water introduced in washing and to use the concentrated solution for the precipitation of a new batch of platinum before treating it to recover its valuable metal content.

METHOD *q* (CHEMICAL).

The palladium that is recovered by the addition of zinc and hydrochloric acid, as explained in method *j* (p. 9), may contain platinum that has not been precipitated. Its quantity, however, should be small, so that a separation, if one is desired, can be effected by heating with dilute nitric acid (1 to 3) the washed precipitate of palladium containing platinum; this will dissolve the palladium and leave the platinum as a residue which is recovered by filtration. If the residue is not small it will doubtless contain palladium that

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was not dissolved by the nitric acid treatment. To recover the platinum metals from this residue, dissolve in aqua regia and repeat the procedures given in *p* and *q*. The palladium is recovered from the filtered solution by evaporating to dryness with hydrochloric acid, extracting with water and acid, and adding zinc as explained in method *j*.

METHOD *r* (CHEMICAL).

If it be desirable to separate the palladium from any copper that may be present (which would be precipitated by method *j*), the following procedure may be used:

The precipitate containing finely divided copper and palladium or other platinum metal is roasted at red heat for an hour or more. Roasting changes the copper to a compound that is soluble in dilute sulphuric acid but leaves the platinum metals insoluble. The roasted material is warmed with successive portions of dilute sulphuric acid (1 to 5), filtered, and washed, first with the dilute acid and then with hot water. This treatment will remove the copper and leave the platinum metal as a residue.

A method that may be used to precipitate platinum metals free from copper is as follows:

Sodium carbonate is cautiously added to the solution, contained in a large dish, until neutral litmus paper is turned blue when dipped into it. The foaming of the solution will be so vigorous that constant stirring is advised. The sodium carbonate should be added gradually and each addition should be dissolved before the next is introduced, so that when the neutral point is reached (when the litmus paper turns blue) the addition can be stopped at once. An excess does no harm except that it will require more reagents. Formic acid is added until neutral litmus paper dipped in the solution turns red; then a few ounces more are added and the solution is boiled in a covered beaker until the precipitate formed coagulates. This will take about one-half hour. The material is then filtered; the palladium and platinum are caught on the filter paper and washed with distilled water to which a few drops of formic acid have been added. The filtrate should be boiled again with addition of more formic acid to see if the precipitation has been complete.

METHOD *s* (CHEMICAL).

The complete separation of iridium and platinum is so difficult that to attempt it is not advisable. If, however, such a separation is required the following methods may be used:

The material, which may contain any or all of the metals given in the table, is melted with silver to make the ratio of silver to platinum metals 15 or more to 1 and the ratio of silver to gold about 3 to 1, and granulated. (See "General Information," p. 2.)

The platinum-iridium-silver alloy obtained in cases 19, 20, 21, and 23 is treated as given in methods *a*, *b*, and *c* to remove silver and the

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solution containing most of the platinum is treated as in methods *i* and *j* or *p*.

A rough separation of the platinum and iridium in the residue may be made by treating it with successive portions of dilute aqua regia (1 to 1), as given in method *m*, page 10, dissolving most of the platinum and a little iridium, which may be recovered together as given in methods *i* and *j*. The residue will consist of iridium with a little platinum.

The products of the previous separation may be treated to separate the platinum and iridium, as will be explained later, but a more satisfactory procedure is to treat the platinum-iridium residue by a method that may be used whenever platinum and iridium are present in the absence of the other platinum metals.

The metal is melted with ten times its weight of pure lead in a covered graphite crucible in which is also placed enough powdered wood charcoal to cover the melt about 1 inch. The heating is conducted in a furnace and should be continued at red heat for about two hours. After the alloy has cooled it is removed and the charcoal washed off. The metal is then treated with successive portions of dilute nitric acid (1 to 5) during four or five hours (it is well to let it digest overnight). The solution, which contains the lead and some platinum, is separated by decantation through a filter; the residue, containing iridium and platinum, is washed with dilute nitric acid and then with hot water. The filtrate and washings are evaporated until crystals begin to form; then sulphuric acid is added until no further precipitation takes place, a little more being added to be sure of an excess. The white precipitate containing part of the lead as sulphate is removed by filtration and washed with hot water. The filtrate is evaporated on a sand bath until copious white fumes come off; then it is cooled and water is added. The cold solution is filtered and the white residue containing the rest of the lead is washed with water. The platinum may be recovered from the solution by procedures given in *i* and *j* or *p*. The residue from the nitric acid extraction containing the iridium and the rest of the platinum is treated for several hours with a mixture of 1 part nitric acid, 4 parts hydrochloric acid, and 9 parts water at a temperature of 80° C. It is well to let this reaction go overnight. The residue is filtered and washed with hot water and is then melted again with lead and treated as before to remove the small quantity of platinum that may still be present. The filtrate and washings are treated as given in *i* and *j* or *p* to recover the rest of the platinum.

The following method may be used to separate platinum and iridium when they are in solution, as in the rough separation given previously. The aqua regia solution containing platinum and iridium is evaporated to dryness, moistened with hydrochloric acid and again evaporated to dryness, and then heated for four hours at 130° C. This temperature should be maintained within 5° and can be accomplished by using a constant-temperature electric oven. By this treatment the iridium is changed to such a condition that it will not be precipitated with the platinum in the next operation. The residue is moistened with hydrochloric acid and dissolved in the least quantity of water. Ammonium chloride is then added until the solution is saturated; after settling for several hours the precipitated platinum salt is removed by decantation through a filter and washed with a saturated solution of ammonium chloride. The residue is then ignited to platinum sponge. The small amount of iridium that may still be present may be separated by treating the sponge with aqua regia as explained before in the rough separation. The filtrate from the precipitation of the platinum salt contains iridium and a small amount of platinum. These metals are recovered together by the procedure given in *j* and may be more completely separated by the method given above which starts by fusing the metals with ten times their weight of lead.

If the granules contain platinum, iridium, palladium, and silver, as in cases 24, 25, and 26, they are treated by the procedure given for the iridium-silver alloy; the palladium goes with the silver and the two are recovered by *a*, *b*, *d*, *i*, and *j*. The residual platinum and iridium are recovered as given above.

If iridium, platinum, palladium, gold, and silver are present the procedure is the same as that given above except that the rough separation method given in the first part of this section is used so that the gold will be dissolved by aqua regia. The residue of platinum and iridium and the platinum metals recovered from the aqua regia solution by method *j*, after the removal of the gold by method *n*, are treated for the separation of platinum and iridium by fusing with lead as explained previously in this section.

METHOD *t* (SMELTING METHOD).

The smelting method, which may be used when the quantity of foreign matter is large, can not be explained in such a way that an inexperienced operator can use it. It is included, however, for the benefit of those who are competent.

The concentrates are mixed with silver (enough to give a ratio of silver to gold of 3 to 1 and of silver to platinum metals of 15 to 1), borax glass, and test lead so as to form a mixture containing about 27 per cent concentrates, 70 per cent lead, and 3 per cent borax glass. This mixture is placed in a scorifier and covered with as much test lead as was used in the mixture. If the quantity of copper is high a little silica is added. The charge is fluxed, scorified, poured, and cupelled as for gold and silver. The molten material is then granulated (see "General Information," p. 2) and treated by the method suited to its valuable metal content as indicated in the table. Some iridium may be lost in the crucible and on the cupel as this metal does not form an alloy with the lead but is held mechanically by it.

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